
Approved For Release
2009/08/26 :
CIA-RDP88-00904R000100110

Third United Nations
International Conference
on the Peaceful Uses
of Atomic Energy



# EXPERIMENTAL PRODUCTION OF STABLE ISOTOPES

I.G.Gverdtziteli, T.A.Gagooa, G.N.Muskhelishvili
U.V.Nikolaev, E.D.Oziashvili, G.A.Thevzadze

## Introduction

To develope works on stable isotopes application a pilot plant producing boron, nitrogen, oxigen, carbon, neon, argon, krypton and other isotopes has been organized in Tbilissi. Isotope separation is carried out by means of distillation, chemical exchange and mass-diffusion methods. Experimental production technological cycle also includes the preparation of initial products to feed boron isotopes separating devices and the synthesis of a number of compounds on th e base of boron, nitrogen, oxigen and other isotopes.

The basic building of the pilot plant is a fifteen-storey tower of the 63 metres height. Column type separating devices are placed on its verticals. Mass-diffusion cascades and auxiliary equipment are situated on its floors. The sufficient height of the tower permits to set columns of cascade one above another; in such a way as to realize material transport between columns through the special dosing devices without piping pump application. It's evident that such a system of f lux distribution appreciably increases separating equipment operation reliabilit y. The four-storey building adjoins upon the tower part. There are placed there: a control-room where all the separating processes automatic control systems are concentrated; initial products producing devices; enriched raw material treatment devices and isotopic composition and chemical analysis control laboratories too.

A general sight of the production building with its tower part is given in the figure I.

## Production Cycle Obtaining Compounds on the Boron-IO and Boron-II Bases.

Technological process general diagram which shows an interrelation between separate cycles is performed in the figure 2. The technological process includes:

366

I. Production of boron trifluoride $BF_3$ and its dimethyl ether complex $(CH_3)_2O \cdot BF_3$;

2. Boron isotope separation by distillation $BF_3$ and exchange distillation $(CH_3)_2O \cdot BF_3$ methods.

3. Converting of the enriched feed into the elemental boron, boron acid and other compounds.

Boron trifluoride is obtained by acidic method (adjustment I) from the reaction:

$$6KBF_4 + B_2O_3 + 6H_2SO_4 = 8BF_3 + 6KHSO_4 + 3H_2O.$$

The purity of $BF_3$ was 99%. The major impurities are: $SO_2$, and $SiF_4$. A part of the boron trifluoride is gone to feed columns, separating boron isotopes by low-temperature distillation—$BF_3$ (adjustment 4), the rest of $BF_3$ is supplied to the device 2 to obtain its dimethyl ether complex. Here dimethyl ether of industrial production is used; the purity of which is 99,8%. The waste of the $BF_3$ producing process is neutralized in the apparatus 3 and is casted off. To produce boron isotopes ( $B^{10}$ and $B^{11}$ ) a number of devices is equipped; they consist of the three separating cascades to obtain boron by the exchange distillation method of the compound $(CH_3)_2O \cdot BF_3$ /I,2/ and columns , separating boron isotopes by $BF_3$ distillation method. /3,4,5/

I. Cascade device with 25kg boron output yearly with $B^{10}$ — 85% concentration consists of the two columns 5 and 6. The diameters of the first and second cascade columns are I28 and 70 mm; the length of the packed part is 2I,7 and 22m accordingly. The $B^{10}$ concentration in the lower part of the first column is 50% and in the waste it is 8%.

2. The column 7 with 50 kg boron output yearly with $B^{10}$ — 40% concentration has a packed part length of 22,7m and a diameter of I28mm. $B^{10}$ concentration in the waste is 8%.

3. The column 8 is meant for 90kg boron yearly production with $B^{11}$ — 99% concentration. The length of its packed part is 23m, and the diameter of the column is I28mm. The $B^{10}$ concentration in the waste is I8,85%.

The column 7 is fed by the waste flux from the column 5, and the waste flux of the columns 6 and 7 feeds the column 8.

To obtain 85% $B^{10}$ in a form of $BF_3$ the column 4 is provided for the boron trifluoride distillation. The output of the column is 35kg of boron yearly.

The principal calculation parameters of the enriched boron isotope producing devices are given in the table I.

The distinguishing peculiarity of the complex distillating devices in comparison of with $BF_3$ distillation devices is a small value of the permissible reflux density; this small value is stipulated by the limitation of the pressure drop value in the columns, because of the thermal instability of the complex at high temperatures. The necessity of carrying out the complex distillation in vacuum is connected with it too; the pressure in the column condensers is kept to be 150mm of mercury.

Further on in one of the devices operating pressure will be increased to I atm. by means of methyl fluoride recirculation through the columb.

The complex thermal decomposition reduction will permit to increase reflux density and to produce 40kg of $B^{10}$ yearly instead of 25Kg at the pressure 0,15 atm.

It must be pointed out that the further increase of the reflux density and outputs of the distillating devices seems expeditious. In such a case as this, reflux density is limited only by the flooding point. The output advantage in this case will be determined by a character of the enrichment factor E dependance on the temperature. This dependance for $BF_3$ is given in the figure 3. Because of E's slight dependance on the temperature there rises the opportunity of carrying out the $BF_3$ distillation process at the pressures 3-5 atm. This circumstance must lead to the rise of the device output for 40 - 60%. The device parameters, given in the table I, relate to the operation when the pressure within the condenser is I atm.

When developing separating devices an appreciable attention was paid not only to the study of existing packing system efficiency, but to the creation of new ones too. Considering that columns with large diameters (more than 30mm) actually cannot be pre-flooded, new packings have been developed which have relatively high efficiency and do not require any pre-flooding.

Packing system , used in exchange distillation columns consists of triangular helice layers with the height of each layer of an order of Icm and capillary gaskets, which are strips of a twice bent metal gauze /6/. Over each helice layer 6-8 gaskets are placed. The width of each gasket is 5 mm, the length is rather less than the column diameter.

The efficiency of this packing system has been determined at the complex distillation in the columns with diameters 47, 74 and I28mm. The HETP values obtained are shown on the fig. 4.In $BF_3$ distillating columns a cap-type packing is applied/7/. The elements of this packing are caps with four sharp teeth, made of metal gauze. They are produced by pressing the pieces of double gauze through the round hole. Pre-flooding is not required.

The figure 5 represents the dependance of efficiency on reflux density when operating without pre-flooding for cap-type packing and for triangular helices with gaskets and without them.

The HETP values have been obtained in the column with the diameter of 94 mm by means of benzene-carbon tetrachloride standard mixture.

The curves in figure 5 show that HETP as well as pressure drop values are minimum for the cap-type packing.

Enriched products $(CH_3)_2O \cdot B^{10}F_3$ and $(CH_3)_2O \cdot B^{11}F_3$ are converted into elemental boron ( apparatus 9,IO). The later is produced by the fused salt electrolysis of potassium chloride KCL and potassium fluoborate $KBF_4$ ;/I/. The product outlet is 80%. The purity of the elemental boron was 92 - 98%. Besides the broad using of $B^{10}F_3$ in neutron-

physical studies and neutron-recorders, it is also a raw material to obtain boron acid, labelled by isotope. Boron acid is obtained by hydrolysis of $BF_3$ (apparatus 2) according to the reaction:

$$4BF_3 + H_2O = 3HBF_4 + H_3BO_3$$

and by further splitting of boron-fluorine-hydrogen acid:

$$HBF_4 + 2CaCO_3 + H_2O = 2CaF_2 + H_3BO_3 + 2CO_2 .$$

## Production Cycle to Obtain Compounds Labelled by Nitrogen 15/.

The general diagram of the cycle is given in the figure 6. The cycle includes:

1. A number of obtaining nodes, internal revolution nodes and waste transport nodes;
2. Separating devices;
3. Enriched product treatment devices.

To obtain nitrogen heavy isotope two processes are used: chemical exchange in the nitric oxide — nitric acid system /8, 9, 10, 11/ and low-temperature distillation of nitric oxide /12, 13, 14/.

In spite of the fact that $N^{15}$ production process by chemical exchange method is sufficiently simple and easily carried out in the industrial scale, it possesses a number of substantial drawbacks; the main of them is: a large amount of sulfurous anhydride expenditure and, accordingly, the formation of a large amount of sulfuric acid in the phase-returning device system. The expenditure for phase-returning makes the dominating part of the general expenditures of the process. More optimum scheme for $N^{15}$ production is combining chemical exchange process in the system $NO \rightleftarrows HNO_3$ with distillation of NO. As we know, when distillating NO simultaneously with nitrogen heavy isotope, oxygen heavy isotope $O^{18}$/13/ can be obtained; and when selecting from the section middle part the enrichments, the concentrated isotope $O^{17}$ can be obtained partially. When applying complex combining distillation and chemical exchange processes, the initial product expenditure is appreciably reduced. Distillation devices are fed by the

waste-flux from the chemical-exchange device.

In connection with the fact, that the low-temperature distillation process technologically is rather complicated, than chemical-exchange process, initially the chemical-exchange device is provided. Afterwards, the main part of $N^{15}$ production will be carried out by nitric oxide distillation method.

The chemical-exchange cascade device diagram for producing 4,5kg of 99% nitrogen yearly is given in the figure 6.

The diameters of the first (2) and second (3) columns are I20 and 26mm; THE lengths of the column packing part are I7,0 and I7,8m. Packing system of the first column represents triangular helices (dimensions of the element: 2,5 X 2,5mm) and gauze gasket layers, placed at every other centimetre. The packing of the second column is represented by triangular helices with element dimensions 2,3 x 2,3mm. The refluxes of the I and 2 columns are 400 and I6cm /min. of IOmolar nitric acid accordingly.

The concentration at the transition point from the I column to the second $C_{k1}$, and, successively, the column lengths are determined to minimize equilibrium time of the cascade. The calculation results in the form of concentration-obtaining time $C_{K2}$ = 98% $N^{15}$ dependance at the end of the second column on the concentration $C_{K1}$ value at the end of the first column are given in the figure 7. The calculation is done for the two values of the first column equivalent theoretical stage height $h_1$ = I2 and 20cm.

As it can be seen from the figure 7, the curve, characterizing this dependance , has sloping minimum in the range of values $C_{K1}$ IO-30%. When reducing $C_{K1}$ below 5% the adjustment time sharply rises.

$N^{15}$ heavy isotope is produced in the form of nitric oxide, nitric acid, free nitrogen and ammonia.

Ammonia, responding high requests of purity, is obtained by calcium nitride hydrolysis. The process consists of three stages:

I.Deoxidation of the nitric oxide to the free nitrogen (apparatus 9);

2. Calcium nitride synthesis (apparatus IO);

3. Calcium nitride hydrolysis (appatus II).

Ammonia's purity in the obtained product is 99,9%. The major impurities are: $N_2$,$H_2$,$H_2O$.The product outlet is 95%.

On the base of nitric oxide, enriched nitrogen $N^{15}$ and oxigen $O^{18}$ isotopes, the production of heavy oxigen water $H_2O^{18}$ and nitric acid $HN^{15}O_3^{19}$ is intended.

## Mass-diffusion.

To produce a whole number of highly enriched isotopes, needed in small amounts, and for the separating small amounts of material, a construction of cascades with I20 mass-diffusion elements and 30 mass-diffusion columns is conjectured. These devices being used for along time in laboratory conditions, showed high reliability and stability of operation /I5,I6/.The main kinds of isotope products obtained in mass-diffusion devices will be neon isotopes $Ne^{21}$, [illegible] $Ne^{22}$, carbon isotope $C^{13}$, argon isotopes $A^{36}$, $A^{38}$, krypton isotope $Kr^{86}$ and others. As an original raw material natural isotopic mixture will be used mainly. In mass-diffusion cascades reenrichment of the isotopes, produced by chemical exchange and distillation method up to the highest concentrations will be carried out. The output of each device, calculated by $Ne^{22}$ with concentration 95—98% is nearly 200gr yearly.

## Isotope and Chemical Composition Control of Production.

Isotopic composition of the compounds on the boron isotope base is measured by two methods: mass-spectrometer method and

nuclear-magnetic resonance. Besides, the samples from the devices of complex-exchange distillation in the form of $(CH_3)_2O \cdot BF_3$ are measured by nuclear-magnetic resonance method; while the samples from the boron trifluoride distillation device in the form of $BF_3$ are measured by means of mass-spectrometer method.

Compound isotopic composition on the base of $N^{15}$ is measured by mass-spectrometer method in a form of compounds: NO and $N_2$ /I8/

The purity of final products $B^{10}$, $B^{11}$, $B^{10}F_3$, $(CH_3)_2O \cdot B^{10}F_3$, $(CH_3)_2O \cdot B^{11}F_3$ and also the purity of feed materials (initial products) is controlled by chemical methods.

## Technological Process Automatic Control System.

Automatic control system of the enterprise must provide with optimum regulation of all the technological processes.

Optimization must take place by means of such parameters, as the concentration of the valuable isotope in final product is, as the maximum output is, as economy is and so on.

These functions must be perfopmed by the controlling electron computer, which operates together with automatic optimizer and electron model of separating columns.

Enterprise automatic control system functional scheme is given in the figure 8.

The automatic regulation of separating devices and initial and final products producing devices is carried out by corresponding control panels with the help of sensing elements D, which controls the technological process, and by means of actuating mechanisms.

The enterprise general control is carried out by the electron computer. It interrogates the sensing elements, after this the data enter the automatic optimizer and together with controlling machine and electron model adjustment , the programme is worked out. The realization of this programme is done by means of commanding device, which sends necessary commands to the corresponding panel of automatic regulation.

To control the technological processes and automatic adjustment system operation serves dispatcher board. Moreover, by means of dispatcher board the introduction of additional data and change of the device operation is performed.

The total system of the enterprise automatic regulation is realized in two stages. The first stage -- formation of separate devices automatic control panels -- includes the development of special sensing elements and actuating mechanisms. The second stage -- formation of an automatic optimizer , electron model and commanding device, which together with the controlling electron computer will make a thorough automation of the enterprise.

At present the first stage of the automation is already realized -- the panels of isotope-separating processes automatic control are formed. Regulation of these processes is carried on by device hydrodynamic parameters. This caused the need of some questions' solvation, which are connected with the measurement; ~~and~~ ; ~~and~~ regulation of aggressive fluid small fluxes and relatively small gas fluxes; the need of regulating reaction zone place in the devices, operating by chemical-exchange method, etc. The expenditure-meters of small fluxes of fluids and gasses are developed; there are developed special actuating mechanism for precise regulating of fluxes, saturated by gasses dissolved in them, and other devices. A particular attention is paid to the reliability and accuracy of regulation . Electron regulators are entirely without contacts and collected on the transistors and magnetic elements.

Fluid flux regulators , operating at continuous, intermittent and quasi-continuous regimes, and also gas flux regulators , secure the control with an error not exceeding $\pm$I,5%, and the major part of the error is due to the expenditure-meters (the error of the regulators themselves are no more than $\pm$ 0,4%).

The reaction zone situation regulation in the reactors is done by self-tuned regulators, which automatically choose a necessary regime for the operation. This provides with the keeping the reaction zone at the assigned place of reactor at aminimum number of regulations.

Circulation regulators in distillation columns provide with keeping the circulation in dependance upon the level of fluid in

the evaporator ; that permits to carry on the separating processes at small hold-ups and entirely excludes the possibility of evaporator overheating.

Other parameter regulators provide with the control with an error not exceeding I% /I8/.

Separating process automatic regulation system includes emergency and warning signal system. Involving a particular importance of signal device reliability a system with thorough self-checking is developed.

Captions

Fig. I -- A general sight of producing building with a tower part.

Fig.2 -- Producing cycle scheme of obtaining compounds on the $B^{IO}$ and $B^{II}$ bases.

I) $BF_3$ producing device.

2) $BF_3$ complex with dimethyl ether producing device.

3) Waste neutralizer.

4) $BF_3$ production device: 85% $B^{IO}$ by distillation.

5,6) the first and the second cascade columns producing 85% $B^{IO}$ by complex-exchange distillation.

7) 99% $B^{II}$ producing column by complex-exchange distillation.

8) 40% $B^{IO}$ producing column by complex-exchange distillation.

9) Tetrafluorideborate potassium producing apparatus.

I0) Electrolytic cell.

II) Boron acid producing apparatus.

Fig.3 -- Boron isotope enrichment factor dependance on temperature at BF distillation.

I - enrichment factor E.I03, 2 - pressure, atm, 3 - temperature, $^{o}K$.

Fig.4 -- Equivalent theoretical stage height dependance on column diameter for packing consisting of triangular helice and capillary gasket segments.

I - ETSH, cm, 2 - diameter, cm.

Fig.5 -- Efficiency of different packings at non-pre-flooding operation.

0 - segments of triangular helices 3,0 x 2,4 ;

- the same packing with capillary gaskets;

x - cap-type packing 4,5/2,8 of double gauze (dashed curves relate to pressure drops)

I - ETSH, 2 - reflux density, $cm/cm^2.min$, 3 - pressure drop mm Hg/m

388

Fig.6 -- Producing cycle scheme of compounds labelled by $N^{15}$
I - Nitrogen oxide absorber.
2,3) The I and 2 columns to produce $N^{15}$ by chemical exchange.
4,5) Phase-returning system
6) Nitric oxide purifying apparatus.
7,8) The I and 2 columns producing $N^{15}$ and $O^{08}$ by distillation.
9) Nitric oxide deoxidation apparatus.
I0,II) Apparatus for calcium nitride synthesis and hydrolysis.
I2) Water and nitric acid producing system from nitric oxide.

Fig.7 -- Concentration $C_{k2}$ 98% $N^{15}$ at the end of the column 2 obtaining time dependance upon the concentration value at the transition point $C_k$ at the height $h_I$ = 20 and I2 cm of the I column stage
I - days, 2 - molar fractions.

Fig.8 -- Enterprise automatic control system functional diagram.
I - from control panel and sensing elements, 2 - from control panel, 3 - unit of interrogation of sensing elements, 4 - automatic optimizer, 5 - electron model, 6 - controlling machine, 7 - dispatcher board, 8 - commanding device, 9 - to control panels, I0 - to the unit of sensing elements interrogation, II - separation unit No.I, I2 - control panel No I, I3 - from sensing elements of separation unit No 2, I4 - control panel No 2, I5 - to the actuating mechanizms of separation unit No 2, I6 - from sensing elements of separation unit i, I7 - control panel i, I8 - to actuating mechanisms of unit i, Д - sensing element ДК - sensing element of isotope concentration, ИМ - actuating mechanism.

Table I

## Device Parameters to Produce Boron Isotopes

| separation method | device | | packing | column diameter mm | HETP | column length: enrichment section | column length: recovery section | liquid reflux density in cm³/min onto 1 cm² of column cross section | reflux density in gr. of boron an 1 cm² area of column cross section | concentration $B^{10}$ %: enrichment section | concentration $B^{10}$ %: recovery section | pressure drop mm. of mercury | fluxes mol/day-night: product | fluxes mol/day-night: waste | fluxes mol/day-night: feeding | boron losses output % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| exchange distillation $(CH_3)_2OBF_3$ | cascade to produce 85% $B^{10}$ | the second the first column | triangular helices 3,5×3,0mm | 128 | 7,2 | 11,88 | 9,72 | 1,27 | 0,140 | 50 | 8 | 140 | 16,2 | 49,8 | 66 | 25 |
| | | | triangular helices 3,2×2,8mm | 70 | 5,5 | 11,94 | 10,18 | 1,30 | 0,143 | 85 | 18,85 | 160 | 6,85 | 18,15 | 15 | |
| | columns to produce 99% $B^{11}$ | | triangular helices 3,5×3,0mm | 128 | 7,2 | 15 | 8 | 1,27 | 0,140 | 1 | 18,85 | 150 | 21,52 | 13,89 | 35,41 | 86 |
| | columns to produce 40% $B^{10}$ | | triangular helices 3,5×3,0mm | 128 | 7,2 | 6,34 | 16,42 | 1,18 | 0,130 | 40 | 2 | 148 | 13,8 | 12,5 | 26,3 | 50 |
| distillation $BF_3$ | columns to produce 85% $B^{10}$ | | cap-type | 57 | 3,5 | 22,33 | 9,33 | 8 | 1,92 | 85 | 8 | 350 | 10,23 | 62,36 | 72,59 | 35 |

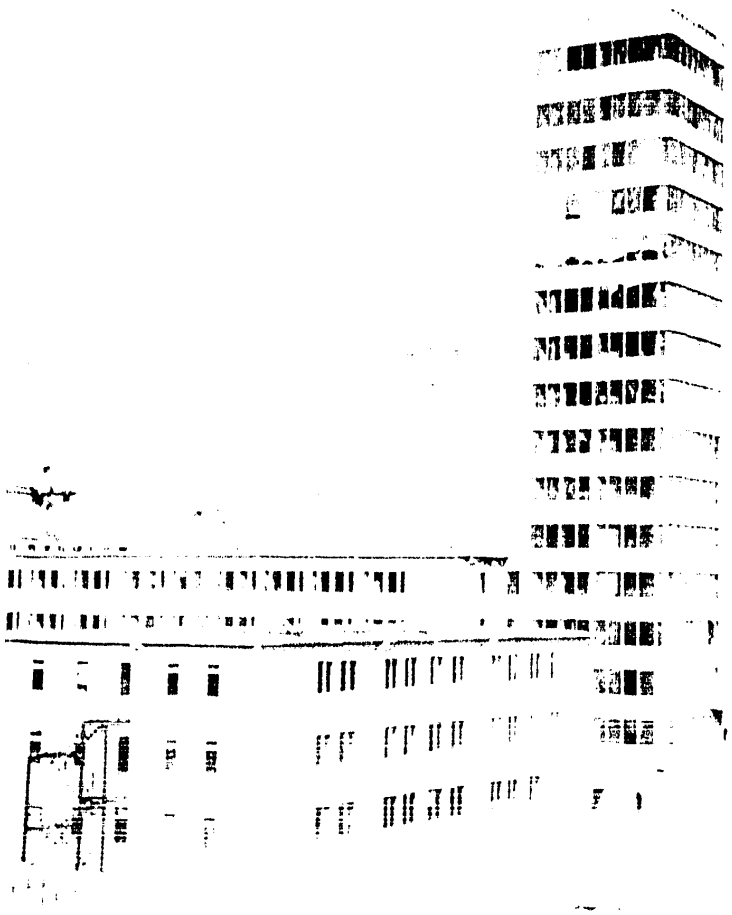

Fig. 1

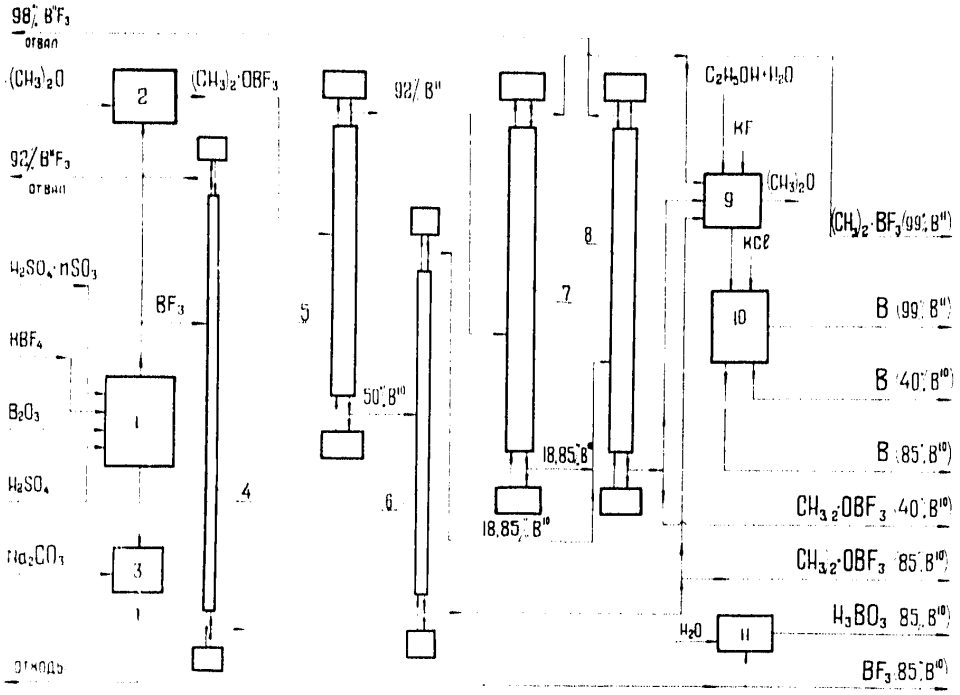


Fig. 2

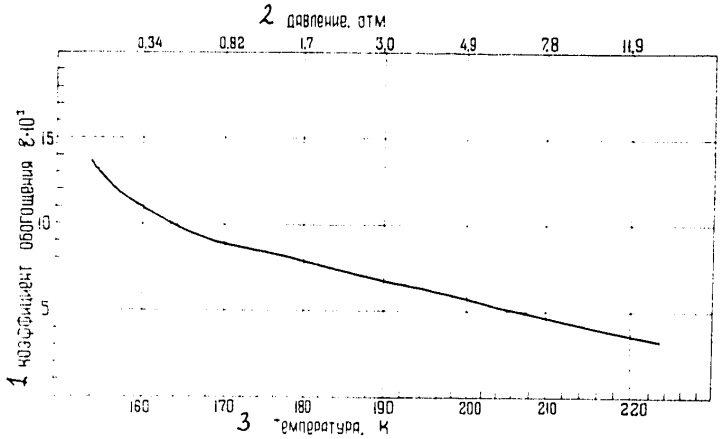


Fig. 3

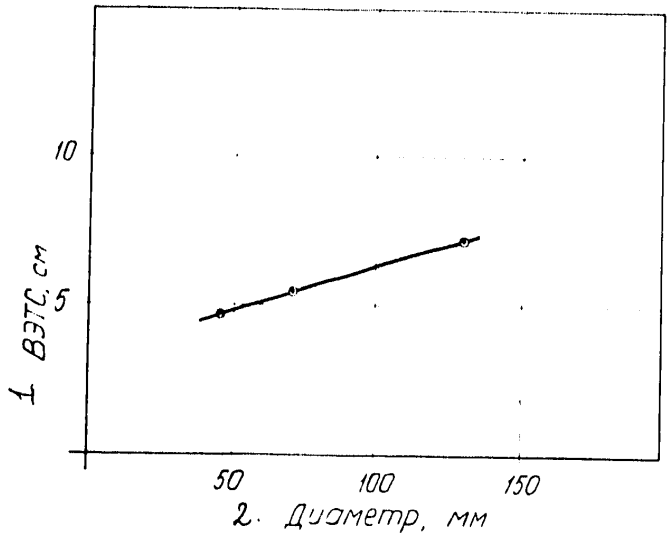


Fig. 4

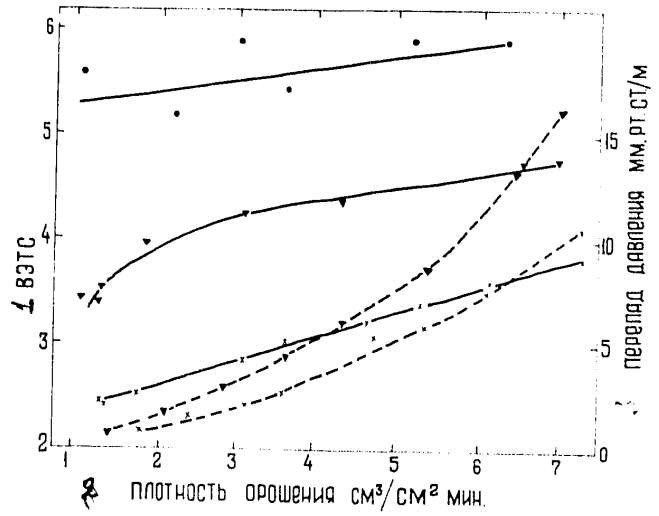


Fig. 5

3 8 5

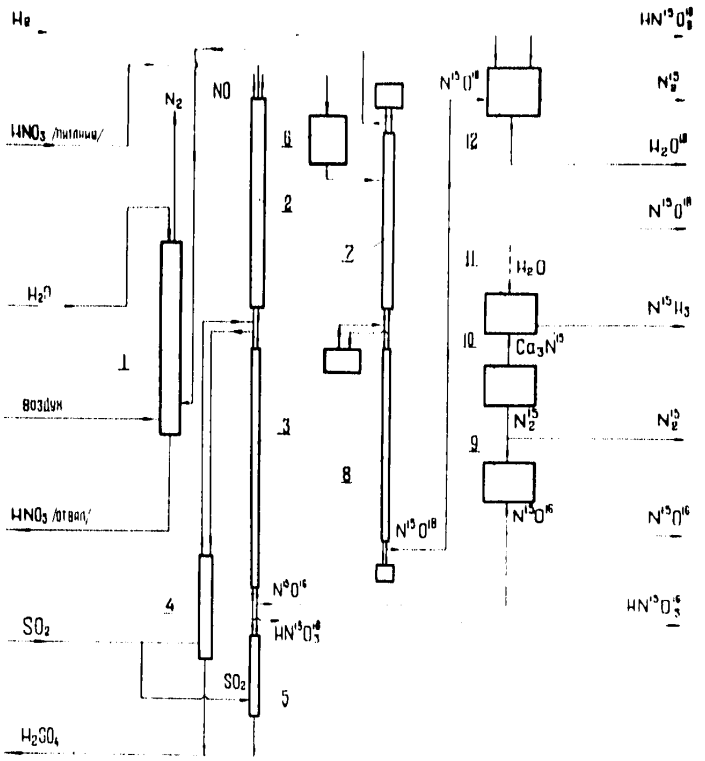


Fig. 6

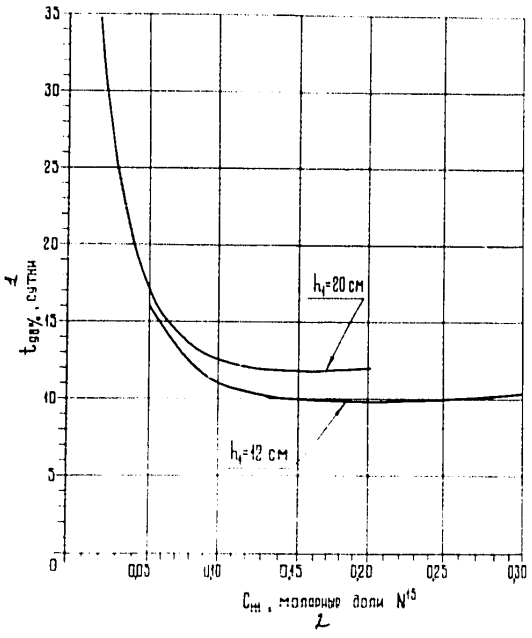


Fig. 7

386

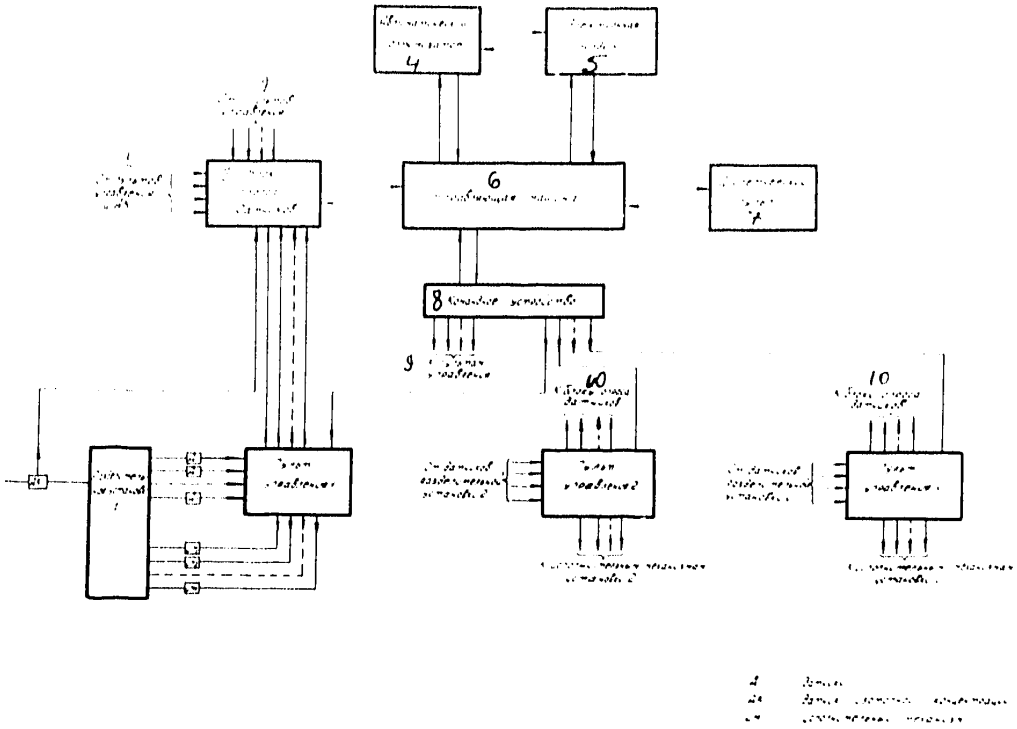


Fig. 8

388